

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-286933

(43)Date of publication of application : 04.11.1997

(51)Int.Cl.

C09D 5/16  
C09D 5/16  
C09D129/10  
C09D143/04  
C09D193/04  
C09D201/02

(21)Application number : 08-217161

(71)Applicant : KANSAI PAINT CO LTD

(22)Date of filing : 19.08.1996

(72)Inventor : TAGI YOICHI  
ISOZAKI OSAMU  
NAGAYAMA SHIGEO  
HANADA TAKAYUKI  
YONEHARA YOICHI

(30)Priority

Priority number : 08 33610 Priority date : 21.02.1996 Priority country : JP

## (54) ANTIFOULING COATING COMPOSITION

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain the subject composition comprising a metal carboxylate resin having a free hydroxyl group and an antifouling agent, exhibiting an excellent antifouling effect, and useful for forming antifouling coating films on ships and marine structures.

**SOLUTION:** This antifouling composition contains (A) a resin represented by the formula: Rp-COOM-OH (Rp is a base resin; M is a divalent metal atom) and having a metal carboxylate group in the molecule, and (B) an antifouling agent as effective components. The component A can be obtained by reacting the resin having a carboxyl group in the molecule with a divalent metal oxide or hydroxide in the presence of a small amount of water. The component B is preferably compounded in an amount of approximately 100-300 pts.wt. per 100 pts.wt. of the component A.

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

## \* NOTICES \*

JPO and NCIPPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## CLAIMS

---

## [Claim(s)]

[Claim 1] The following general formula (I)



(RP shows base resin among a formula and M shows a divalent metal atom, respectively.) The antifouling paint constituent characterized by making the resin (A) and the stain proofing agent (B) which have metal carboxylate in the intramolecular expressed into an active principle.

[Claim 2] The constituent according to claim 1 whose resin (A) is what a divalent metaled oxide or a divalent metaled hydroxide is made to react to the resin which has a carboxyl group in intramolecular under existence of little water, and is obtained.

[Claim 3] The constituent according to claim 1 or 2 whose divalent metal atom in resin (A) is 1 chosen from copper, zinc, calcium, magnesium, and iron, or 2 or more.

[Claim 4] Claim 1 which contains rosin further as a resinous principle thru/or the constituent of three given in any 1 term.

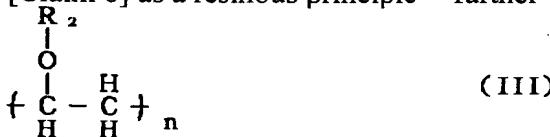
[Claim 5] As a resinous principle, it is the following general formula (II) further.

[Formula 1]



(-- R1 shows the monovalence hydrocarbon group of C1 - C40 among a formula.) -- constituent of 3 claim 1 containing the resin which has an average of two acid anhydrous radicals expressed at least in 1 molecule thru/or given in any 1 term.

[Claim 6] as a resinous principle -- further -- the following general formula (III) -- [Formula 2]



(-- R2 shows the alkyl group of C1 - C3 among a formula.) -- constituent of 3 claim 1 containing the polyvinyl alkylether expressed thru/or given in any 1 term.

[Claim 7] As a resinous principle, it is the following general formula (IV) further.

[Formula 3]



(-- among a formula, R4 shows the same or the alkyl group of C6 - C12 which may be different from each other, and, as for n, R3 shows the integer of 100-10000 for a hydrogen atom or a methyl group mutually.) -- constituent of 3 claim 1 containing the poly dimethyl alkyl silyl (meth)acrylate expressed thru/or given in any 1 term.

---

[Translation done.]

## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the antifouling paint constituent which can form the paint film which uses it for a vessel and the offshore structure and prevents living thing dirt in detail about an antifouling paint constituent.

#### [0002]

[Description of the Prior Art] Before, in order to prevent the corrosion by adhesion of marine organisms, such as acorn shells, a bryozoan, a sea squirt, and algae, and the fall of the NAV rate of a vessel, the antifouling paint which comes to blend a stain proofing agent with binder resin is painted by the rejection water space of a vessel or the offshore structure.

[0003] For example, although the coating which uses TAFUNA -, rosin, a plasticizer, etc. as a binder was known, the paint film by this coating had the fault to which the antifouling effectiveness falls, when insoluble matter increased in long-term seawater immersion.

[0004] Moreover, various coatings which use as a binder the resin which has metal salt structure are also studied and put in practical use by intramolecular as an antifouling paint. Although the most famous thing as resin that has metal salt structure in intramolecular is carboxylate of tin, since this thing has a toxic problem, copper, zincky carboxylate, etc. are mainly examined in recent years. Although the paint film by this coating maintains antifouling property by the elution of the paint film by hydrolysis of a metal salt part, it has fully come to control the rate of dissolution of this paint film. As for the resin which furthermore has metal salt structure in intramolecular, a hydroxyl group does not usually remain. By the conventional synthetic approach, when a hydroxyl group exists in these resin, it is for producing gelation at the time of composition. However, the resin by this synthetic approach tended to become cost quantity.

#### [0005]

[Means for Solving the Problem] As a result of inquiring wholeheartedly that the above-mentioned fault should be solved, this invention persons found out forming the antifouling paint film excellent in the coating constituent containing the metal carboxylate resin and the stain proofing agent which have a free hydroxyl group, and reached this invention.

[0006] According to this invention in this way, it is the following general formula (I).

RP-COOM-OH (I)

(-- RP shows base resin among a formula and M shows a divalent metal atom, respectively.) -- the intramolecular expressed is provided with the antifouling paint constituent characterized by making into an active principle the resin (A) and the stain proofing agent (B) which have metal carboxylate.

[0007] The resin (A) used by this invention is resin which has metal carboxylate in the intramolecular expressed with the above-mentioned general formula (I), and can be obtained by making a divalent metaled oxide or a divalent metaled hydroxide react to the resin which has a carboxyl group in intramolecular under existence of little water.

[0008] It is suitable to make it react with the oxide of a divalent metal or a hydroxide in 0.1-1 mol to one mol of carboxyl groups in resin in the above. Moreover, the amount of 0.1-1 mol is suitable for the amount of the water used to one mol of carboxyl groups. Since superfluous water will dissociate if structural viscosity is [ the amount of this water used ] discovered by less than 0.1 mols, resin thickens and one mol is exceeded on the other hand, it is not desirable.

[0009] It is suitable to add 0.5 - 5% of the weight of water, the oxide of a divalent metal to make it add, or a hydroxide as the concrete synthetic approach of the above-mentioned resin (A) to the resin which has a carboxyl group in intramolecular, and to make it react at the temperature of 50-200 degrees C for 1 to 20 hours. When the system of reaction becomes muddy by existence of water, the minimum polar solvents are added. As these polar solvents, an alcoholic system, a ketone system, an ester system, an ethers solvent, etc. are mentioned, and by this use, the system of reaction becomes transparency, for example as a reaction progresses, although powder-like metallic compounds do not dissolve at first.

[0010] Although it can be especially used without a limit as the oxide or hydroxide of the above-mentioned divalent

metal, one of the oxides or hydroxides of copper, zinc, calcium, magnesium, and iron are desirable from points, such as cost, toxicity, and reactivity.

[0011] As resin which has a carboxyl group in the above-mentioned intramolecular, although anythings of a vinyl polymerization object, polyester, polyurethane, and natural resin etc. are usable, the vinyl polymerization object which comes to copolymerize carboxyl group content monomers, such as an acrylic acid (meta), and other vinyl monomers, such as acrylic-acid alkyl ester and styrene, from the degree of freedom of presentation fluctuation is suitable.

[0012] As for the resin (A) obtained as above-mentioned, it is desirable for the acid numbers to be 80-200, and it is desirable 1,000-50,000, and for number average molecular weight to be in the range of 3,000-20,000 preferably. Moreover, it is suitable for this resin (A) that -10-60 degrees C of glass transition temperature are in the range of 10-40 degrees C preferably.

[0013] Although the above-mentioned resin (A) is used as a resinous principle in this invention, rosin (C) can be used together and contained further. as this rosin -- gum rosin and wood rosin -- all can be used and these denaturation objects can also be used. What is marketed as the rosin which contains an abietic acid at a high rate among these, for example, WW rosin, is suitable. Mallein-ized rosin, FUTARU-ized rosin, etc. can be mentioned as a denaturation object.

[0014] the blending ratio of coal of the above-mentioned resin (A) and rosin (C) -- both amount of total indicator solid content -- (Resin A) 5-99 % of the weight and (Rosin C) 95- the range of (Resin A) 10-75 % of the weight and (Rosin C) 90-25 % of the weight is preferably suitable 1% of the weight. the blending ratio of coal of resin (A) -- 99 % of the weight -- exceeding (rosin being less than 1 % of the weight) -- the reinforcement of a paint film may be small, and the dissolved water in fuel of a paint film may become less enough, and the long-term antifouling holdout of a paint film may fall On the other hand, a paint film becomes easy to break, when the blending ratio of coal of resin (A) becomes hard too much at less than (rosin exceeds 95 % of the weight) 5 % of the weight, and a paint film becomes weak and carries out impasto of the paint film.

[0015] Moreover, at this invention, it is the following general formula (II) further as a resinous principle.

[0016]

[Formula 4]



[0017] (-- R1 shows the monovalence hydrocarbon group of C1 - C40 among a formula.) -- in 1 molecule, at least, the resin (D) which it has an average of ten pieces at least preferably can be used together, and an average of two acid anhydrous radicals expressed can be contained. Inside R1 of a formula As for the monovalence hydrocarbon group of C1 expressed - C40, an alkyl group, a cycloalkyl radical, an aryl group, an aralkyl radical, a polycyclic type terpene radical, etc. are included.

[0018] As resin (D) which has the above-mentioned acid anhydrous radical, the resin manufactured, for example by following approach (1) - (4) can be used.

[0019] (1) What carboxylate content resin and the compound (it abbreviates to a "acid chloride" below.) which has a COCl radical are made to react, and is obtained, (2) Resin which has a COCl radical (it abbreviates to "acid chloride-ized resin" below.) After making the thing and (3) carboxylate content monomer which a carboxylate content compound is made to react and are obtained, and an acid chloride react and obtaining an acid anhydrous radical content monomer, What is obtained by carrying out copolymerization of this thing to other vinyl monomers homopolymerization or if needed, (4) What is obtained by carrying out copolymerization of this thing to other vinyl monomers homopolymerization or if needed after making the monomer which has a COCl radical, and a carboxylate content compound react and obtaining an acid anhydrous radical content monomer.

[0020] As the above-mentioned carboxylate content resin, although resin, such as a vinyl system, a polyester system, and an alkyd system, can be used It is a vinyl system preferably. Specifically Carboxyl group content monomers, such as an acrylic acid (meta), a crotonic acid, and an itaconic acid, The vinyl copolymer which comes to copolymerize the vinyl monomer of others, such as acrylic-acid alkyl ester and styrene Resin which is neutralized with basic compounds, such as tertiary amine and a sodium hydroxide, and is obtained; (meta) the resin which comes to copolymerize a carboxylate content monomer and other vinyl monomers, such as tertiary amine of an acrylic acid and a salt with alkali metal, is mentioned. Moreover, the above-mentioned acid chloride is a chloride of monocarboxylic acid compounds, such as an acetic acid, a lauric acid, oleic acid, palm oil fatty acid, a benzoic acid, and rosin, and the above-mentioned acid chloride-ized resin is the homopolymer of for example,  $\text{CH}_2 = \text{CHCOCl}$ , or a copolymer with other vinyl monomers. As the above-mentioned carboxylate content compound, the tertiary amine of the above-mentioned monocarboxylic acid compound and a salt with alkali metal are mentioned, for example.

[0021] As a monocarboxylic acid compound component of the above-mentioned acid chloride or a carboxylate content compound, when the benzoic acid which is not permuted [ a permutation or ] is used, there is an advantage that it can give fungiproofness and disinfectant to a paint film.

[0022] The above-mentioned polymerization reaction and an acid anhydrous radical composition reaction can be conventionally manufactured by the well-known approach, respectively, for example, 60-200-degree C heating can

perform this polymerization reaction under existence of a polymerization catalyst in an inactive organic solvent, and a room temperature or heating can perform an acid anhydrous radical composition reaction in an inactive organic solvent.

[0023] As for the resin (D) obtained as above-mentioned, it is desirable 3,000-200,000, and for number average molecular weight to be in the range of 5,000-80,000 preferably.

[0024] the blending ratio of coal in the case of the above-mentioned resin (D) being hydrolysis nature like said resin (A), self-scouring being shown if it is made the film, and using these together -- both amount of total indicator solid content -- (A)1-99 % of the weight and (D)99- the range of (A)25-75 % of the weight and (D)75-25 % of the weight is preferably suitable 1% of the weight.

[0025] Moreover, at this invention, it is the following general formula (III) further as a resinous principle.

[0026]

[Formula 5]



[0027] ( -- R2 shows the alkyl group of C1 - C3 among a formula.) -- the polyvinyl alkylether (E) expressed can be used together and contained. This polyvinyl alkylether (E) is alkyl ether of polyvinyl alcohol, and has fine water solubility. The solubility to water is molecular weight and R2. It is determined by the carbon number, the range of 10-10,000 ppm is desirable, the ethyl ether of C2 is specifically suitable, and it is C1. With methyl ether, water solubility is C3 highly. It is desirable to adjust solubility to this within the limits combining three sorts in pro PIRUE-Tell, since water solubility is low.

[0028] the loadings in the case of using together the above-mentioned polyvinyl alkylether (E) with resin (A) -- the (Resin A) 100 weight section -- receiving -- 1 - 30 weight section -- the range of 5 - 20 weight section is preferably suitable. Since drying may be spoiled if this range is crossed, it is not desirable.

[0029] Furthermore at this invention, it is the following general formula (IV) as a resinous principle.

[0030]

[Formula 6]



[0031] ( -- among a formula, in R3, R4 shows the same or the alkyl group of C6 - C12 which may be different from each other, and n shows the integer of 100-10000 for a hydrogen atom or a methyl group mutually.) -- the poly dimethyl alkyl silyl (meth)acrylate (F) expressed can be used together and contained. Inside R4 of a formula As for the alkyl group expressed, a hexyl group, an octyl radical, the dodecyl, etc. are included. As this poly dimethyl alkyl silyl (meth)acrylate (F), what is indicated by JP,5-56765,B, for example is mentioned.

[0032] the blending ratio of coal in the case of using together the above-mentioned poly dimethyl alkyl silyl (meth)acrylate (F) with resin (A) -- both amount of total indicator solid content -- (A)1-99 % of the weight and (F)99- the range of (A)25-75 % of the weight and (F)75-25 % of the weight is preferably suitable 1% of the weight.

[0033] As a stain proofing agent (B) used by this invention, for example A cuprous oxide, thiocyanogen copper, Copper system stain proofing agents, such as copper powder; Ethylene bis(dithiocarbamic acid) zinc, Nitrogen-containing sulfur system stain proofing agents, such as tetramethyl thiuram JISURUFAIDO; Bis(triphenyltin) oxide, Bis(tributyltin) oxide, tributyltin acetate, tributyltin chloride, Triphenyltin hydroxide, triphenyl SUZUBA-SATE-TO, Screw (tributyltin) alpha and alpha'- a jib -- organic tin system stain proofing agent; nitril system compounds, such as ROM succinate, -- A germicide, zinc oxides, etc., such as a benzothiazole system compound, triazine compound, a urea system compound, an iso thiazoline system compound, a maleimide system compound, N-halo alkylthio system compound, a tetracyclines compound, and zinc pilus thione, are mentioned. [, such as a pyridine system compound, ]

[0034] It is appropriate for the loadings of the above-mentioned stain proofing agent (B) to consider as 100 - 300 weight section extent to the resin 100 weight section.

[0035] Although the antifouling paint constituent of this invention makes indispensable the above-mentioned resin (A) and a stain proofing agent (B), it may contain further pigments, a plasticizer, a solvent and the other additives used for an antifouling paint, for example, a surface control agent, a dripping stop agent, etc. if needed.

[0036] Especially as an approach of forming a paint film using the coating constituent of this invention, it is not restricted and a well-known approach is used conventionally. concrete -- the underwater structure (for example, a vessel, harbor facilities, a buoy, and a pipeline --) a bridge, a submarine base, a culture network, a fixed net, etc. -- etc. -- a base material front face -- direct or a base material -- a wash primer -- Primers, such as a zinc epoxy system shop primer; An oily anticorrosive, Under coat primers, such as a chlorinated-rubber system and an epoxy system; The

monolayer paint film in which applied intermediate coats, such as a chlorinated-rubber system and an epoxy system, to, respectively, and they were made to form, It can apply to the base material front face in which the double layer paint film in which the coating of a primer and an under coat primer was made to apply and form and the primer, the under coat primer, and the double layer paint film in which carried out sequential paint and the intermediate coat was made to form were prepared with means, such as brush coating, spray coating, roller coating, and immersion.

Generally 40-500 micrometers of within the limits of 80-300 micrometers are preferably suitable for the coverage as desiccation thickness. Although desiccation of a paint film can be performed at a room temperature, stoving may be performed at the temperature to about 100 degrees C if needed.

[0037]

[Example] Hereafter, an example is given and this invention is further explained to a detail. In addition, especially the "section" and "%", unless it refuses, the "weight section" and "% of the weight" are meant.

[0038] Added the zinc oxide 8 section, the butanol 5 section, and the water 1 section in the 50% butyl-acetate solution 100 of the copolymer of the number average molecular weight 10,000 which comes to copolymerize the monomer mixture which consists of the example of manufacture manufacture 1 acrylic-acid 7.2 section of resin (A), the methyl methacrylate 50 section, and the ethyl acrylate 42.8 section section, it was made to react at 120 degrees C for 10 hours, and the transparent resin solution (A-1) of 50% of solid content was obtained. According to the IR in this resin, absorption of zinc carboxylate had appeared greatly in 1630cm-1.

[0039] Added the cellosolve 100 section, the calcium-hydroxide 2 section, and the water 2 section in the polyester resin 100 section of number average molecular weight 3,500 and the acid number 56 which comes to add a succinic anhydride to the polyester resin which has a hydroxyl group at the end which consists of example of manufacture 2 adipic acid / neopentyl glycol / trimethylol propane, it was made to react to it at 100 degrees C for 10 hours, and the transparent resin solution (A-2) of 50% of solid content was obtained. According to the IR in this resin, absorption of calcium carboxylate had appeared greatly in 1560cm-1.

[0040] The methacrylic-acid 86 section and the deionized water 50 section were taught to 4 opening flask furnished with example of manufacture manufacture 3 agitator of resin (D), a thermometer, and reflux tubing, and the water solution which dissolved the sodium-hydroxide 40 section in the deionized water 50 section was dropped and added there. When generation of heat was subsided, the toluene 400 section was added and heated, and the water separator removed water under reflux. Then, it cooled to the room temperature and the acetyl-chloride 78.5 section was dropped, after the 1-hour reaction, it filtered and the transparent and colorless monomer solution was obtained.

[0041] Subsequently, the monomer solution 100 above-mentioned section which taught the xylene 90 section to the same another flask as the above, and was condensed to 50% of solid content there, The mixed liquor of the methyl methacrylate 50 section and the azobisisobutyronitril 3 section is dropped over 2 hours, and it is made to react at 100 degrees C under stirring. The mixed liquor of the 1 hour after azobisisobutyronitril 1 section and the xylene 10 section was made to react in addition over 1 hour, and the resin solution (D-1) which is the light yellow viscous liquid object of 50% of solid content was obtained.

[0042] Taught the toluene 100 section and the butyl-acetate 107.6 section to the same flask as the example 3 of example of manufacture 4 manufacture, and the mixed liquor of the acrylic-acid 7.2 section, the n-butyl methacrylate 52.8 section, the ethyl acrylate 40 section, and the benzoyl peroxide 2 section was dropped there over 2 hours, it was made to react at 100 degrees C under stirring, and the mixed liquor of the 1 hour after benzoyl peroxide 1 section and the toluene 50 section was made to react in addition over 1.5 hours. The potassium-hydroxide water-solution 11.2 section was added to 80 degrees C after [ cooling ] 50%, the temperature up was carried out to them, and the water separator removed water under stirring. It cooled at 50 degrees C after that, the benzoyl-chloride 14.1 section was added, and the resin solution (D-2) which is the light yellow viscous liquid object of 30% of solid content was obtained by the decantation after 3-hour stirring.

[0043] The dimethylhexylsilylmethacrylate 68 section and the toluene 32 section were taught to the same flask as the example 3 of example of manufacture manufacture 5 manufacture of resin (F), the bottom azobisisobutyronitril of stirring 0.5 section was added, it heated at 60 degrees C by the nitrogen purge, heating stirring was carried out at this temperature for 8 hours, and the resin solution (F-1) which is a transparent and colorless viscous liquid object in 68% of solid content was obtained.

[0044] In the example 5 of example of manufacture 6 manufacture, the resin solution (F-2) which is a transparent and colorless viscous liquid object was obtained by 61% of solid content by the same actuation as the example 5 of manufacture except using the dimethyl DESHIRU silyl methacrylate 61 section instead of the dimethylhexylsilylmethacrylate 68 section.

[0045] Mixed distribution of the resin solution (A-1) 50 section obtained in the example of the creation example 1 above-mentioned manufacture of an antifouling paint, the chlorinated paraffin 2.5 section, the cuprous-oxide 30 section, the red ochre 2 section, the EROJIRU #200 (trade name, product [ made from DOITSUDEGUSA ], silica powder) 0.5 section, and the xylene 11 section was carried out in paint conditioner -, and the antifouling paint was obtained.

[0046] In examples 2-12 and one to example of comparison 7 example 1, each antifouling paint was obtained like the example 1 except considering as the combination shown in Table 1. In addition, the notes in Table 1 are as follows.

[0047] "RUTONA-RU A25" : The Bayer make, polyvinyl ethyl ether, (Note 1) Liquefied object (notes 2) "PURIO light S5B" : Made in Goodyear, Incorporated, Styrene butadiene copolymer (notes 3) "EROJIRU #200" : The Degussa AG make, To the test panel with a magnitude of 100x300x3.2mm which gave the anticorrosive coat with the silica powder coating trial BINIRUTA-RU system coating, the antifouling paint obtained above was applied so that it might be set to 100 micrometers by desiccation thickness, and it was dried, and each color card was obtained to it. The following performance test was presented with the obtained color card. A result is shown in Table 1.

[0048] (Test method) Each color card was immersed in the place with a depth [ of the Suruga bay / in seawater ] of 1m, and the rate of living thing dirt surface ratio (%) estimated the antifouling property of 6, 12, and 18 or 24 months after.

[0049]

[Effect of the Invention] According to the antifouling paint constituent of this invention, the paint film which demonstrates the outstanding antifouling effectiveness can be formed.

[0050]

[Table 1]

表 1

|                         | 実 施 例 |     |     |     |     |     |     |     |     |     |     |     |
|-------------------------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                         | 1     | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
| 樹脂溶液 (A-1)              | 50    |     | 25  |     | 25  | 25  |     | 50  |     | 25  | 25  |     |
| " (A-2)                 |       | 50  |     | 25  |     |     | 25  |     | 50  |     |     | 25  |
| ロジン (65%キシレン溶液)         |       |     | 19  | 19  |     |     |     |     |     |     |     |     |
| 樹脂溶液 (D-1)              |       |     |     |     | 25  |     | 25  |     |     |     |     |     |
| " (D-2)                 |       |     |     |     |     | 41  |     |     |     |     |     |     |
| ルトナール A 25 (81)         |       |     |     |     |     |     |     | 1.5 | 5   |     |     |     |
| 樹脂溶液 (F-1)              |       |     |     |     |     |     |     |     |     | 18  |     |     |
| " (F-2)                 |       |     |     |     |     |     |     |     |     |     | 20  | 20  |
| ナトリウムS5B(40%キシレン溶液)(82) |       |     |     |     |     |     |     |     |     |     |     |     |
| 塩素化パラフィン                | 2.5   | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| 亜酸化銅                    | 30    | 30  | 30  | 30  | 30  | 30  | 30  | 30  | 30  | 30  | 30  | 30  |
| ベンガラ                    | 2     |     | 2   | 2   | 2   | 2   | 2   | 2   | 2   | 2   | 2   | 2   |
| 炭酸カルシウム                 |       |     | 3   |     |     |     |     |     |     |     |     |     |
| エロジル # 200 (83)         | 0.5   | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 防汚性 (%)                 | 6ヶ月   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
|                         | 12ヶ月  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
|                         | 18ヶ月  | 10  | 5   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
|                         | 24ヶ月  | 30  | 10  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |

[0051]

[Table 2]

表1 (つづき)

|                           | 比較例  |     |      |      |      |     |     |
|---------------------------|------|-----|------|------|------|-----|-----|
|                           | 1    | 2   | 3    | 4    | 5    | 6   | 7   |
| 樹脂溶液 (A-1)                | 50   |     |      |      |      |     |     |
| " (A-2)                   |      | 50  |      |      |      |     |     |
| ロジン (65%キシレン溶液)           |      |     | 25.7 |      | 38.5 |     |     |
| 樹脂溶液 (D-1)                |      |     |      |      |      | 50  |     |
| " (D-2)                   |      |     |      |      |      |     |     |
| ルトナールA 25 (#1)            |      |     |      |      |      |     |     |
| 樹脂溶液 (F-1)                |      |     |      |      |      |     | 40  |
| " (F-2)                   |      |     |      |      |      |     |     |
| ブリオナイトSSB(40%キシレン溶液) (#2) |      |     | 20.8 | 62.5 |      |     |     |
| 塩素化パラフィン                  |      |     | 2.5  | 2.5  | 2.5  | 2.5 | 2.5 |
| 亜酸化銅                      |      |     | 30   | 30   | 30   | 30  | 30  |
| ベンガラ                      |      |     | 2    | 2    | 2    | 2   | 2   |
| 炭酸カルシウム                   |      |     |      |      |      |     |     |
| エロジル #200 (#3)            | 0.5  | 0.5 | 0.5  | 0.5  | 0.5  | 0.5 | 0.5 |
| 防汚性 (%)                   | 6ヶ月  | 60  | 70   | 0    | 10   | 0   | 0   |
|                           | 12ヶ月 | 100 | 100  | 5    | 50   | ハガレ | 0   |
|                           | 18ヶ月 | 100 | 100  | 10   | 100  | ハガレ | 10  |
|                           | 24ヶ月 | 100 | 100  | 20   | 100  | ハガレ | 20  |

[Translation done.]